

Solid State Structural Studies of Some New Derivatives of $\text{HN}(\text{SO}_2\text{CF}_3)_2$ and HOTeF_5



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14. ABSTRACT The šcisoidŠ form is less common. In the CCDC, only 6 structures show this conformation whereas the štransiodŠ form occurs in 15 remaining structures The šcisoidŠ conformation results from stronger cation-anion interaction šCisoidŠ observed exclusively when anion is chelated to the metal center The štransoidŠ form dominates in structures containing a šfreeŠ anion NO structure known containing both šcisoidŠ AND štransoidŠ geometry					
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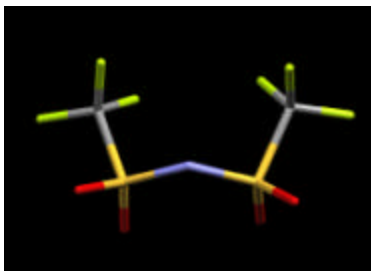


Dr. Fook S. Tham

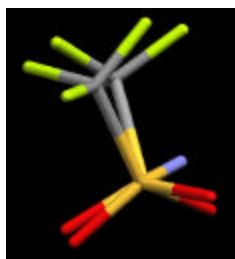
Department of Chemistry, University of California, Riverside CA 92521



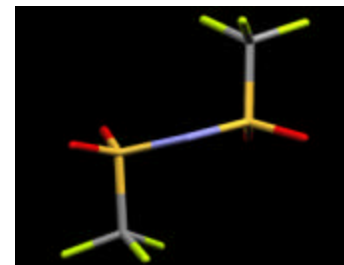
Coordination & isomerism in $N(\text{SO}_2\text{CF}_3)_2$ (NTf)



“Cisoid”



**C-S--S-C
“torsion”**



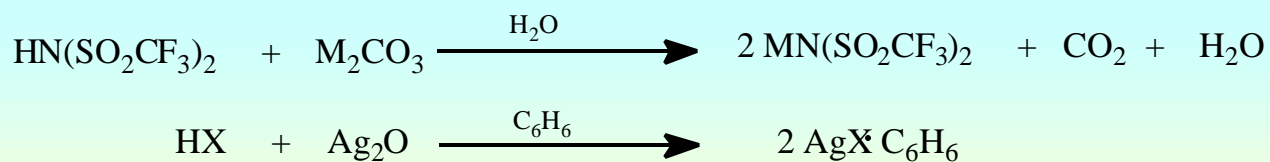
“Transoid”

- ✓ The “cisoid” form is less common. In the CCDC, only 6 structures show this conformation whereas the “transoid” form occurs in 15 remaining structures
- ✓ The “cisoid” conformation results from stronger cation-anion interaction
- ✓ “Cisoid” observed exclusively when anion is chelated to the metal center
- ✓ The “transoid” form dominates in structures containing a “free” anion
- ✓ NO structure known containing both “cisoid” AND “transoid” geometry

DesMarteau, Pennington *et al.*, Solid State Sciences, 2002, 4, 1535-1545



Synthesis of metal(I) derivatives



X = OTeF₅ or NTf

These salts are colorless crystalline materials. Some turn amorphous with time

nTe-O (cm⁻¹): IR (Ra) at ~865 (860)

n_{as}SO₂ (cm⁻¹): IR (Ra) at
~1320(~1328)

¹H NMR: C₆H₆ peak at 7.6-7.7 ppm

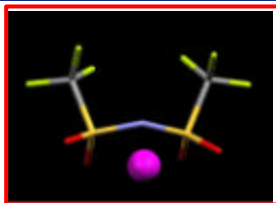
Uncoordinated benzene: 7.3

¹⁹F NMR: ~-78 ppm (CF₃)

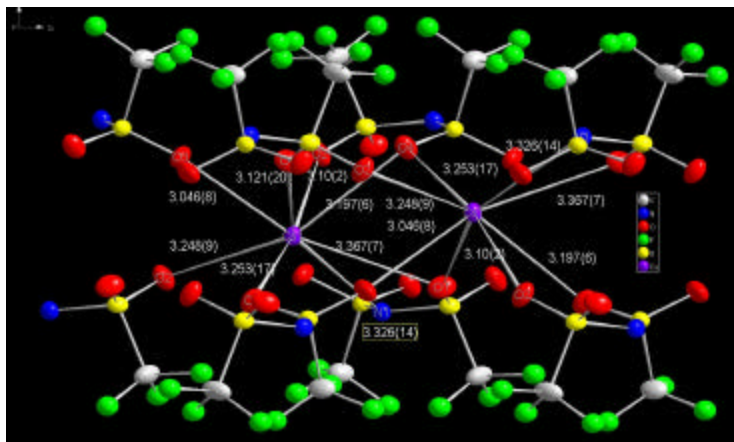
- ✓ These salts are colorless and crystalline.
- ✓ Recrystallization from iso-propylalcohol gave anhydrous salts.
- ✓ Some of these salts turn amorphous with time



Structure of $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



$\text{CsN}(\text{SO}_2\text{CF}_3)_2$



Monoclinic $C2/c$ [$\beta = 91.92(1)^\circ$]

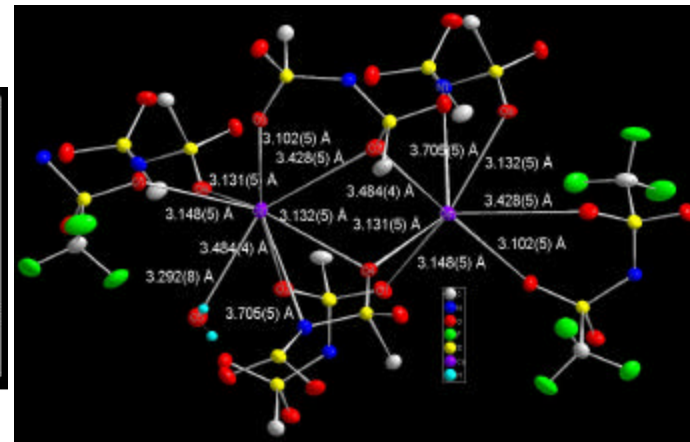
$a = 22.509(12)$, $b = 7.029(4)$, $c = 13.519(7)$ [Å]

Volume (Å³) = 2137.5(19), $Z = 8$, $T = 298$ K

$R1 = 0.0399$, $S = 1.024$



$\text{CsN}(\text{SO}_2\text{CF}_3)_2 \cdot \text{H}_2\text{O}$



Tetragonal $I-4$

$a = 16.903(1)$, $c = 7.8933(6)$ [Å]

Volume (Å³) = 2255.2(3), $Z = 6$, $T = 298$ K

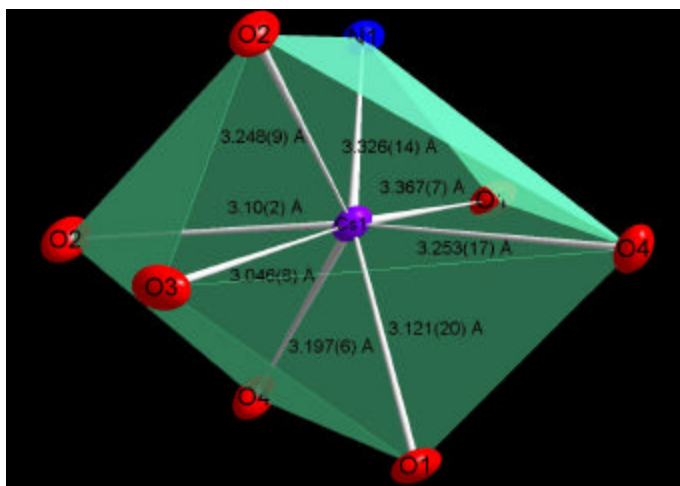
$R1 = 0.0307$, $S = 1.20$



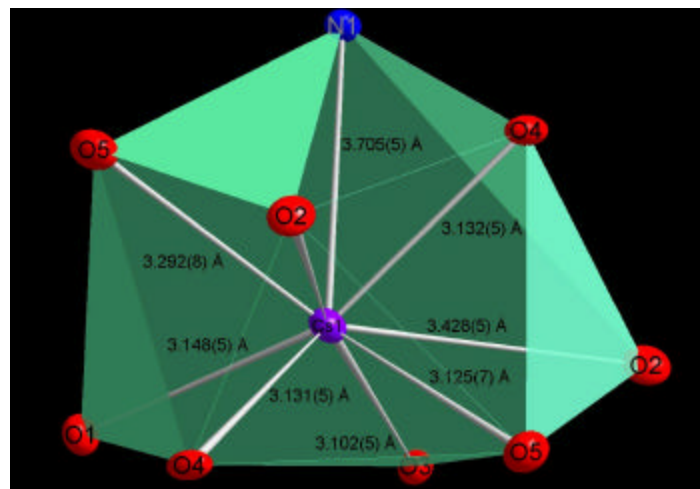
Coordination environment of Cs in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Octa-coordinated with a short Cs-N bond



Nona-coordinated with a long Cs-N bond

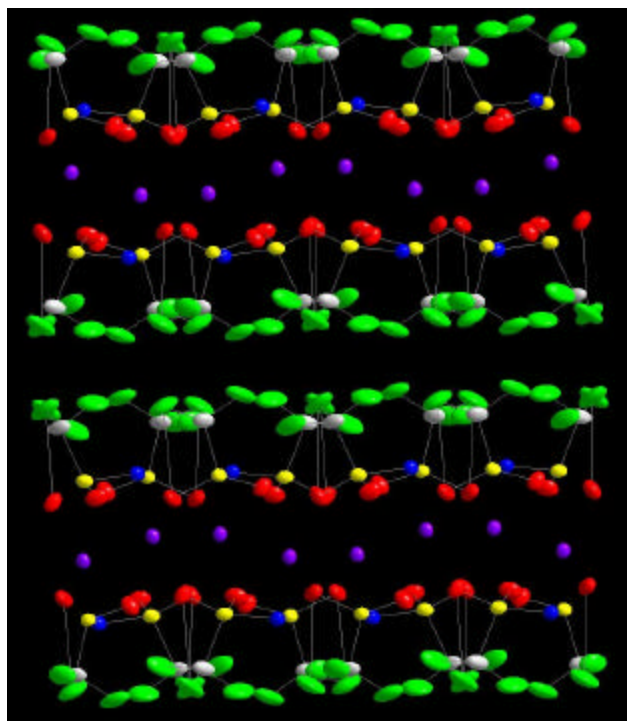




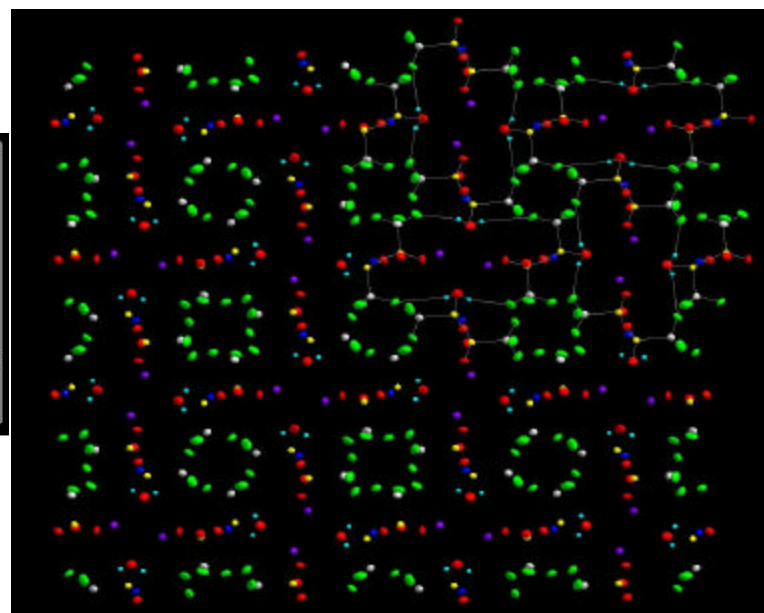
Crystal packing in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Hydrophobic and hydrophilic Layering

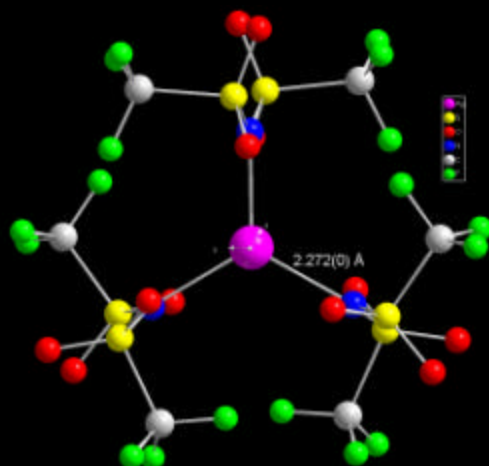


“Swiss cheese” Tunnel/channel structure





Polymorphism in silver bis(trifluoromethylsulfonyl)imide

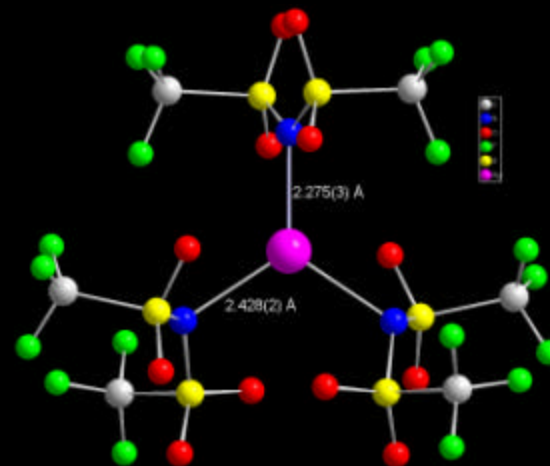


Similar trans Ag-N distances, angles = 120°

Trigonal $P\text{-}3_1c$

$a = 7.510(6) \text{ \AA}$, $c = 8.119(7) \text{ \AA}$

$Z = 6$, $T = 298 \text{ K}$



Cis (long), trans (short) Ag-N distances,
angles NOT 120°

Orthorhombic $Pbca$

$a = 7.510(6) \text{ \AA}$, $b = 15.729(12) \text{ \AA}$, $c = 8.119(7) \text{ \AA}$

$Z = 4$, $T = 298 \text{ K}$

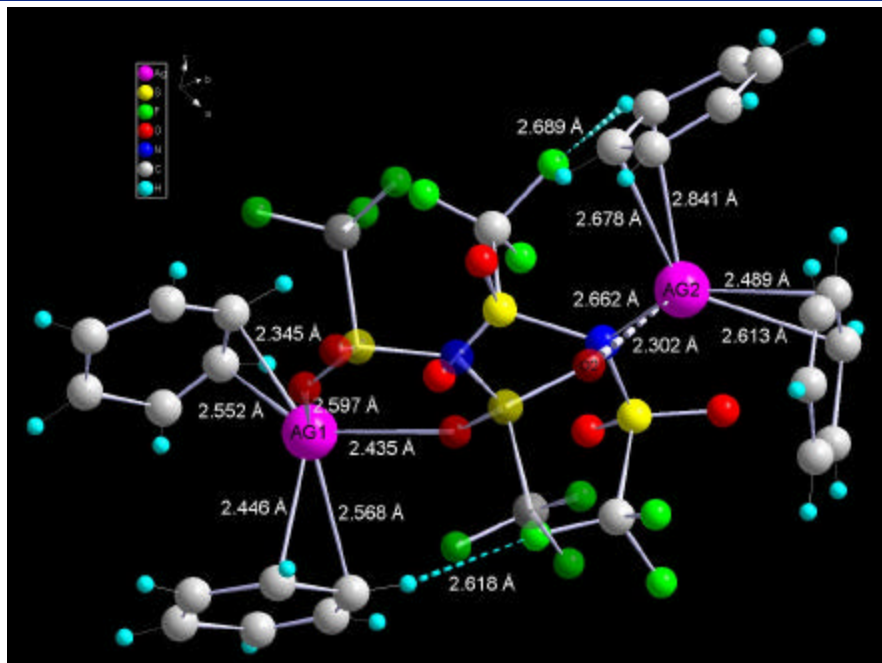
Steric control of tricoordination around Ag is known in $[\text{Ag}(\text{CpPh}_2\text{P})_3]^+ [\text{BF}_4]^-$

However, binary tricoordinated silver salts are unknown

Baiada, A.; Jardine, F. H.; Willett, R.D. *Inorg. Chem.* **1990**, 29, 4805



Structure of $[AgN(SO_2CF_3)_2(C_6H_6)_2]$



Triclinic $P-1$

$a = 7.6704(13) \text{ \AA}$, $b = 8.4295(14) \text{ \AA}$, $c = 8.8631(15) \text{ \AA}$,

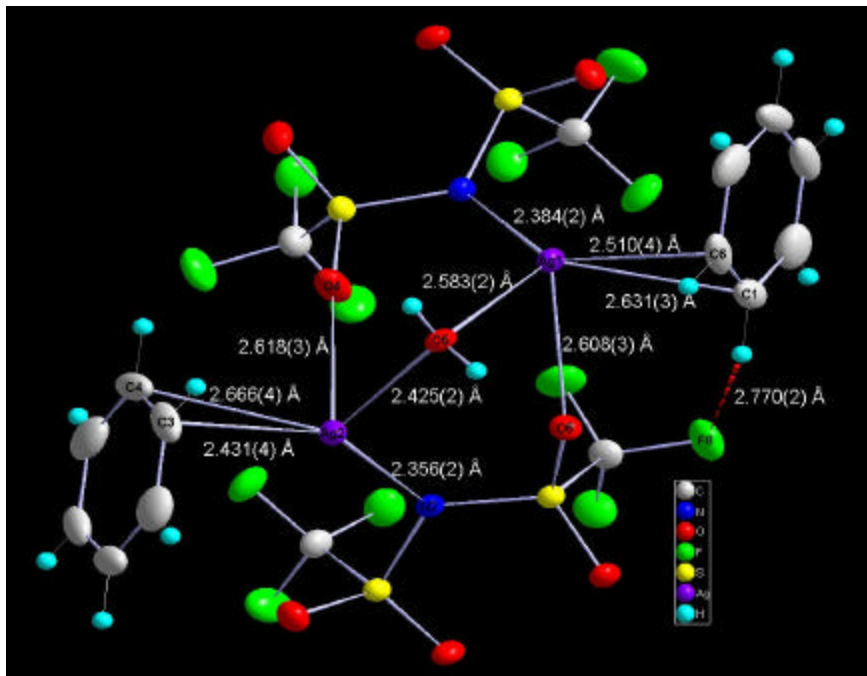
$\alpha = 111.673(3)^\circ$, $\beta = 108.479(3)^\circ$, $\gamma = 97.798(3)^\circ$

$V (\text{ \AA}^3) = 483.89(14)$, $Z = 2$, $T = 298(2) \text{ K}$; $R1 = 0.0432$, $S = 1.114$

- ✓ Dimerization via S-O...Ag bonding (2.302 Å)
- ✓ Long range for unsymmetrical Ag-C bonds (2.345-2.841 Å)
- ✓ $N(SO_2CF_3)_2$ group is “*transoid*”
- ✓ H...F bond distances observed close to sum of van der Waal distance



Structure of $[AgN(SO_2CF_3)_2(C_6H_6)]_2 \cdot H_2O$



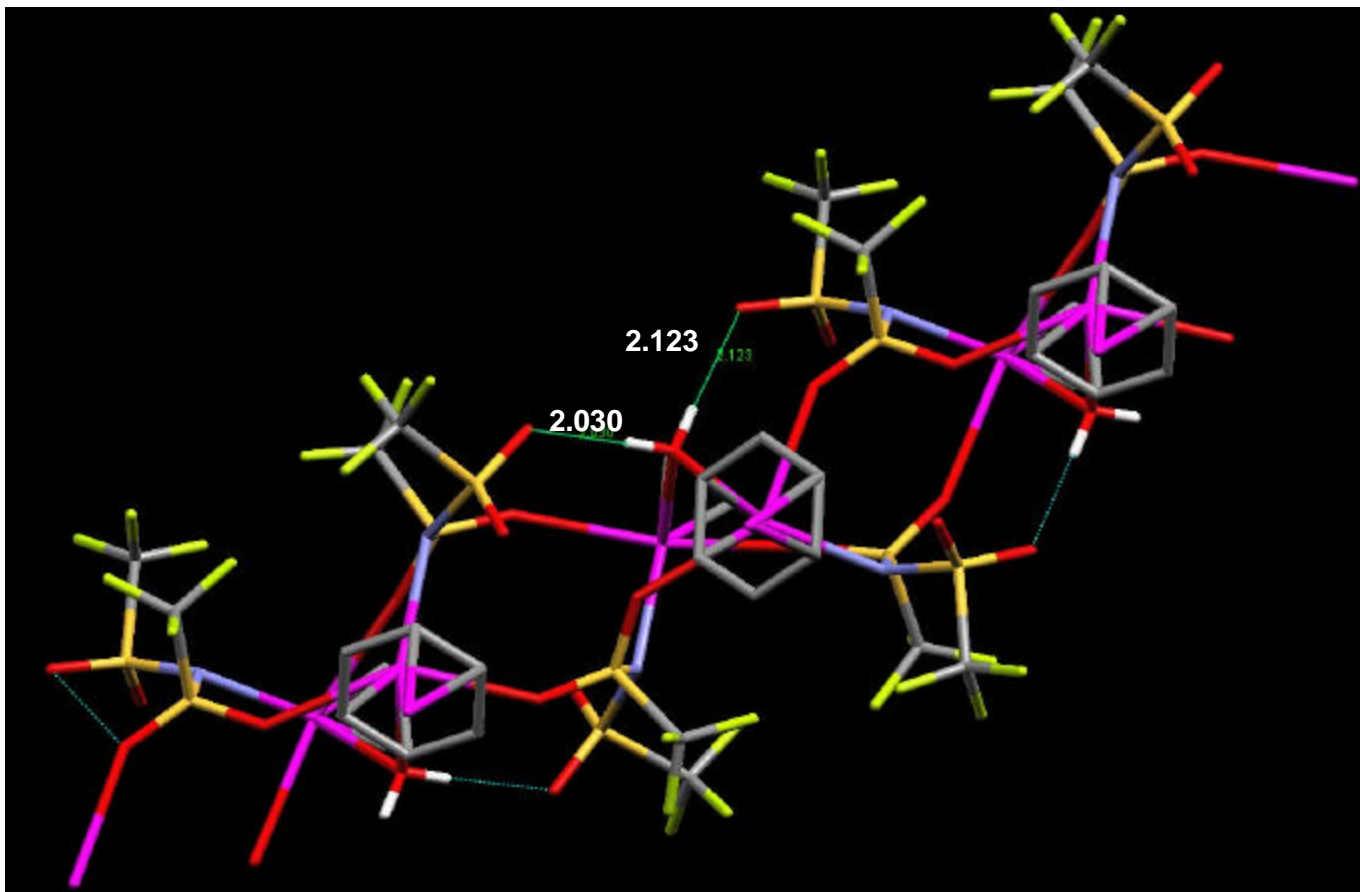
Monoclinic $P2_1/n$

$a = 10.372(1) \text{ \AA}$, $b = 19.823(2) \text{ \AA}$, $c = 12.406(1) \text{ \AA}$, $\beta = 108.536(3)^\circ$,
 $V (\text{ \AA}^3) = 2148.5(5)$, $Z = 8$, $T = 173(1) \text{ K}$; $R1 = 0.0224$, $S = 1.04$

- ✓ $N(SO_2CF_3)_2$ group is both N- as well as O-bonded to silver
- ✓ Water bridges the eight-membered Ag-O-S-N-Ag-O-S-N ring forming two fused six-membered rings.
- ✓ Unsymmetrical Ag-C bonds (2.431-2.666 Å)
- ✓ $N(SO_2CF_3)_2$ group is “*cisoid*”
- ✓ H...F bond distances observed close to sum of van der Waal distance



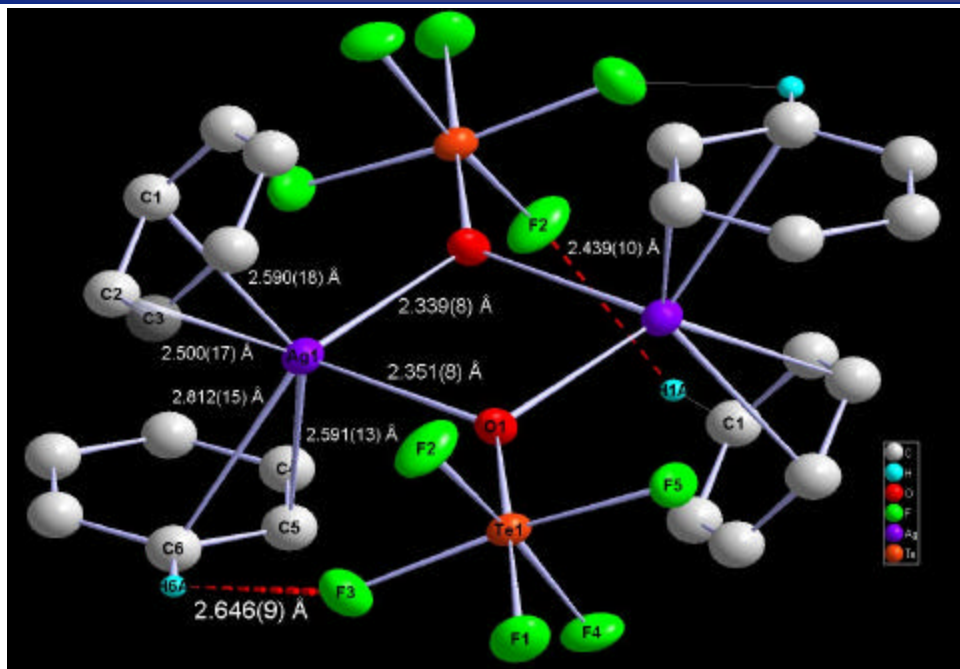
Crystal packing in $[AgN(SO_2CF_3)_2(C_6H_6)]_2 \cdot H_2O$



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Structure of $[AgOTeF_5(C_6H_6)_2]_2$



- ✓ Dimeric structure
- ✓ Unsymmetrical Ag-C bonds
- ✓ Unsymmetrical and very long Te-O bonds
- ✓ H...F bonds observed

Triclinic $P-1$

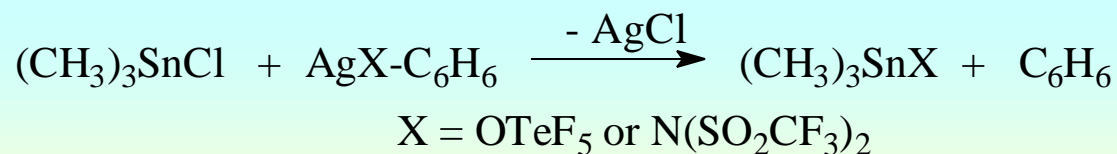
$a = 7.6704(13) \text{ \AA}$, $b = 8.4295(14) \text{ \AA}$, $c = 8.8631(15) \text{ \AA}$,

$\alpha = 111.673(3)^\circ$, $\beta = 108.479(3)^\circ$, $\gamma = 97.798(3)^\circ$

$V (\text{ \AA}^3) = 483.89(14)$, $Z = 2$, $T = 298(2) \text{ K}$; $R1 = 0.0432$, $S = 1.114$



Synthesis of trimethyltin(IV) derivatives: Silver salt metathesis or acidolysis



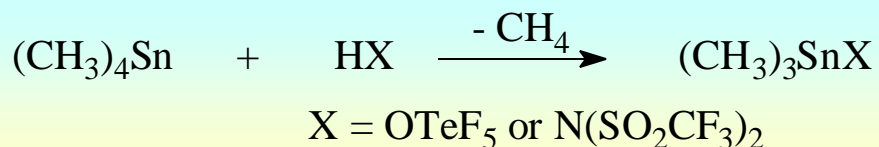
MS shows $[\text{M-CH}_3]^+$ peak

Trimethyltin(IV) teflate can be distilled at 50 °C under vacuum (0.1 T)

$\nu_{\text{Te-O}} (\text{cm}^{-1})$: IR (Ra) at 860 (856)
 $\nu_{\text{Sn-C}} (\text{cm}^{-1})$ IR (Ra): asym: 552 (554); sym 518 (518)

$\nu_{\text{asSO}_2} (\text{cm}^{-1})$: IR (Ra) at 1342(1327)
 $\nu_{\text{Sn-C}} (\text{cm}^{-1})$ IR (Ra): asym: 558 (556); sym 520 (513)

$\nu_{\text{Te-O}} (\text{cm}^{-1})$ F_5TeOCl : IR (Ra) at 551 (554); $\nu_{\text{Te-O}} (\text{cm}^{-1})$ F_5TeOTBA : IR (Ra) at 867 (866);





Synthesis and properties of methyltin(IV) derivatives



- ✓ **Tetramethyltin can be used in large excess to avoid disproportionation**
- ✓ **Reaction by-products can be easily removed under vacuum**
- ✓ **Trialkyltin(IV) derivatives are colorless viscous oils**
- ✓ **Highly sensitive to moisture**
- ✓ **Form complexes with donor solvents.**
- ✓ **Potentially stronger catalysts in organic synthesis compared to TMSOTf (^{119}Sn Chemical shift +162 ppm from TMT)**



Correlating spectroscopy and crystallography



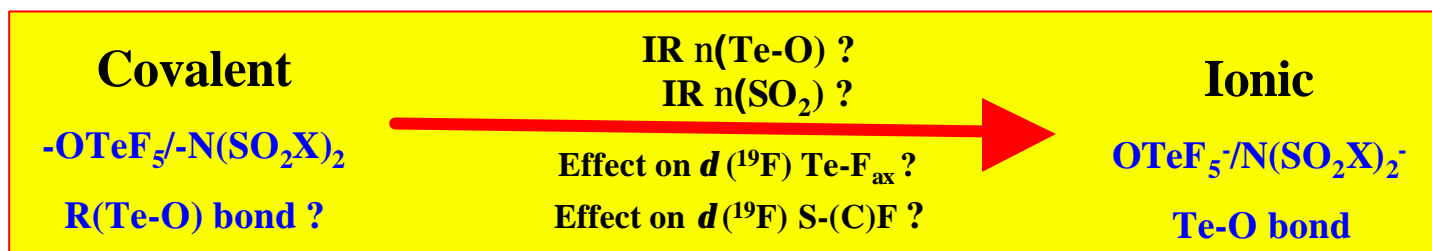
Correlation of $^2J(^{119}\text{Sn}-^1\text{H})$ and C-Sn-C angle (determined from x-ray crystallography) gives the following non-linear relationship:

Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* 1985, 25, 892
Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* 1985, 107, 4546

$$T(\text{C-Sn-C})^\circ = 0.0161 |^2J(^{119}\text{Sn}-^1\text{H})|^2 - 1.32 |^2J(^{119}\text{Sn}-^1\text{H})| + 133.4$$

Correlation of $^1J(^{119}\text{Sn}-^{13}\text{C})$ and C-Sn-C angle (determined from x-ray crystallography) gives the following linear relation:

$$11.4T - 875 = |^1J(^{119}\text{Sn}-^{13}\text{C})|$$





Multinuclear NMR Parameters

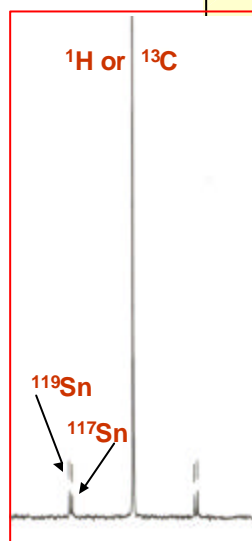


Table 1. ^1H , ^{13}C NMR Spectroscopic Data^a and calculated^{b,c} C-Sn-C angles for $(\text{CH}_3)_3\text{SnX}$ [X = OTeF_5 and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

Solute	Solvent ^d	$\delta(^1\text{H})$ ppm	$^2J(^{119}(\text{Sn})-^1\text{H})$ Hz	$\theta(\text{C-Sn-C})^b$ (°)	$\delta(^{13}\text{C})$ ppm	$^1J(^{119}(\text{Sn})-^{13}\text{C})$ Hz	$\theta(\text{C-Sn-C})^c$ (°)
$(\text{CH}_3)_3\text{SnOTeF}_5$	neat	0.84	59.2 ^e	111.7	0.84	376.9(360.3)	109.8
	CH_2Cl_2	0.79	58.5(55.9)	111.3	0.90	374.0(357.4)	109.6
	acetone	0.69	68.8(65.8)	118.8	1.55	480.4(459.3)	118.9
	CH_3CN	0.66	69.2(66.2)	119.2	1.49	484.6(463.1)	119.3
	DMSO	0.50	69.5(66.6)	119.4	1.05	511.4(490.0)	121.6
$(\text{CH}_3)_3\text{SnOTeF}_5$	AN/ H_2O	0.46	69.6(66.7)	119.5	0.10	508.5(486.0)	121.4
	DMSO/ H_2O	0.43	70.1(68.5) ^e	120.0	0.84	515.5(492.5)	122.0
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat	0.91	63.8(61.6)	114.7	1.6	416.8(400.3)	113.3
	CH_2Cl_2	0.96	62.3(59.9)	113.6	1.4	404.1(387.7)	112.2
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$	DMSO	0.83	72.4(70.0)	122.2	-0.2	528.3(509.9)	123.1
	neat	0.84	64.2(61.6)	115.0	2.1	412.6(394.1)	113.0
	CH_2Cl_2	0.81	64.4(61.8)	115.2	0.8	414.8(395.2)	113.0
	CH_3CN	0.82	70.2(67.1)	120.1	-1.7	489.5(467.6)	119.7
	DMSO	0.48	69.0(67.4)	119.0	0.7	512.2(499.0)	121.6
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	CH_3CN	0.61	69.7(66.7)	119.6	0.10	491.8(470.0)	120.0
	DMSO	1.18	69.8(66.7)	119.7	0.92	512.9(497.2)	121.8

^a NMR spectroscopic data were recorded at 300 K.

^b Calc from relation: $\theta = 0.0161 |^2J(^{119}\text{Sn}-^1\text{H})|^2 - 1.32 |^2J(^{119}\text{Sn}-^1\text{H})| + 133.4$.

^c Calc from relation: $|^1J(^{119}\text{Sn}-^{13}\text{C})| = 11.4 \theta - 875$.

^d Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$.

^e Calculated from center of unresolved ^{119}Sn , ^{117}Sn satellites ($|J_{\text{obs}}| \times 1.023$)



Multinuclear NMR parameters ...continued



Table 2. ^{19}F , ^{119}Sn and ^{125}Te NMR Spectroscopic Data^a of $(\text{CH}_3)_3\text{SnX}$ [$\text{X} = \text{OTeF}_5$ and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

Solute	Solvent ^b	$\delta(^{19}\text{F})$, ppm			$\lambda(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}})$ Hz	$\delta(^{119}\text{Sn})$ ppm	$\delta(^{125}\text{Te})$ ppm	$\delta(^{13}\text{CF}_3)$ ppm	$^1J(^{125}\text{Te}-^{19}\text{F})$, Hz		
		F_{ax}	F_{eq}	$\text{CF}_2/\text{SO}_2\text{F}$					F_{ax}	F_{eq}	Hz
$(\text{CH}_3)_3\text{SnOTeF}_5$	neat	-32.9	-41.9		182.5	270.8 ^c	569.5		3112	3540	
	CH_2Cl_2	-30.3	-38.5		183.0	272.4	564.6		3188	3550	
	acetone	-29.1	-40.6		180.0	96.0	574.9		3020	3558	
	CH_3CN	-29.2	-40.8		179.0	84.2	575.0		3032	3556	
	DMSO	-16.2	-33.8		170.0	40.0	598.7		2712	3666	
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat			55.5		242.5					
	CH_2Cl_2			55.6		248.6					
	DMSO			52.5		32.9					
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$	neat			-78.5		240.2		118.7			320.4
	CH_2Cl_2			-78.8		251.0		118.1			319.8
	CH_3CN			-78.9		44.9		119.4			320.7
	DMSO			-78.6		37.4		120.0			321.7
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	CH_3CN			-79.0		59.0					
	DMSO			-79.1		42.8					

^a NMR spectroscopic data were recorded at 300 K

^b Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$

^c ^{119}Sn NMR shows a peak at 300.7 ppm in HOTeF_5

$^{19}\text{F}_{\text{ax}}$ NMR for TEAOTeF_5 = -25.4 ppm

$\text{B}(\text{OTeF}_5)_3$ = -46.2 (Strauss et al., 1986)



^{119}Sn chemical shifts and anion basicity



- $d(^{119}\text{Sn})$ values lower (more downfield) than +200 ppm show a highly deshielded tin nuclei. Sometimes stronger acids results in relatively higher (upfield) chemical shifts due to close contacts even in solution state:

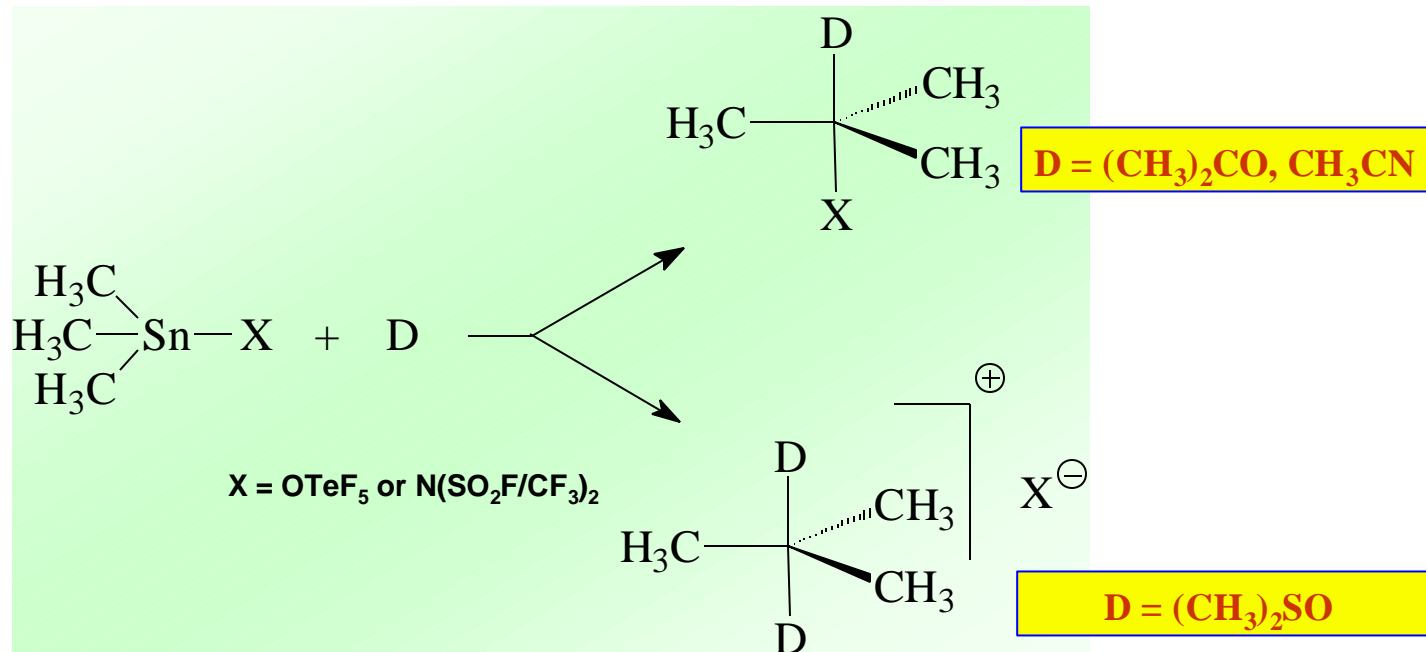
➤ <u>Compound (Me_3SnX)</u>	<u>$d(^{119}\text{Sn})$</u>
$\text{X} = \text{ClO}_4$ (unidentate)	245
$\text{X} = \text{SO}_3\text{CF}_3$ (bidentate)	162

For trimethyltin(IV) derivatives in dichloromethane solution the relative anion basicity can be ordered as:





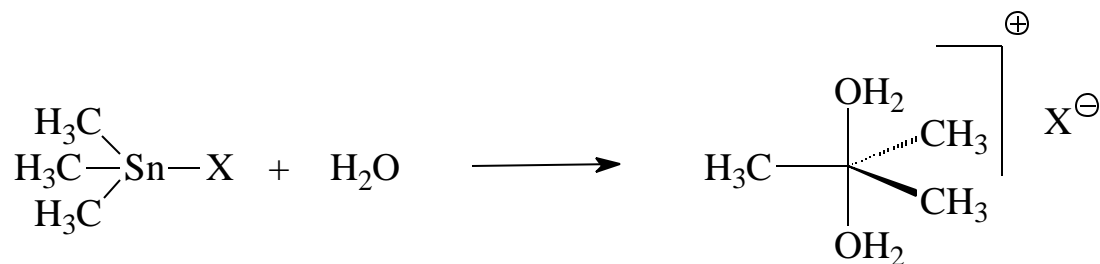
Coordination complex formation with donor solvents



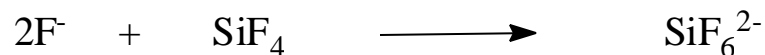
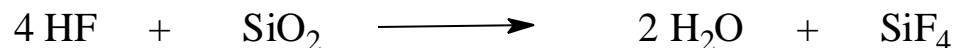
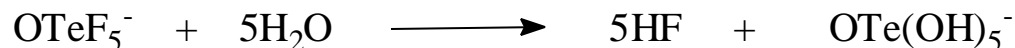
Covalent	IR $\nu(\text{Te}-\text{O})$ increases IR $\nu(\text{SO}_2)$ decreases	Ionic
$-\text{OTeF}_5/-\text{N}(\text{SO}_2\text{X})_2$	$d(^{19}\text{F}) \text{Te}-\text{F}_{\text{ax}}$ is deshielded $d(^{19}\text{F}) \text{S}-(\text{C})\text{F}$ is shielded	$\text{OTeF}_5^-/\text{N}(\text{SO}_2\text{X})_2^-$
Long Te-O bond		Short Te-O bond



Formation of the hydrated trimethylstannyl cation



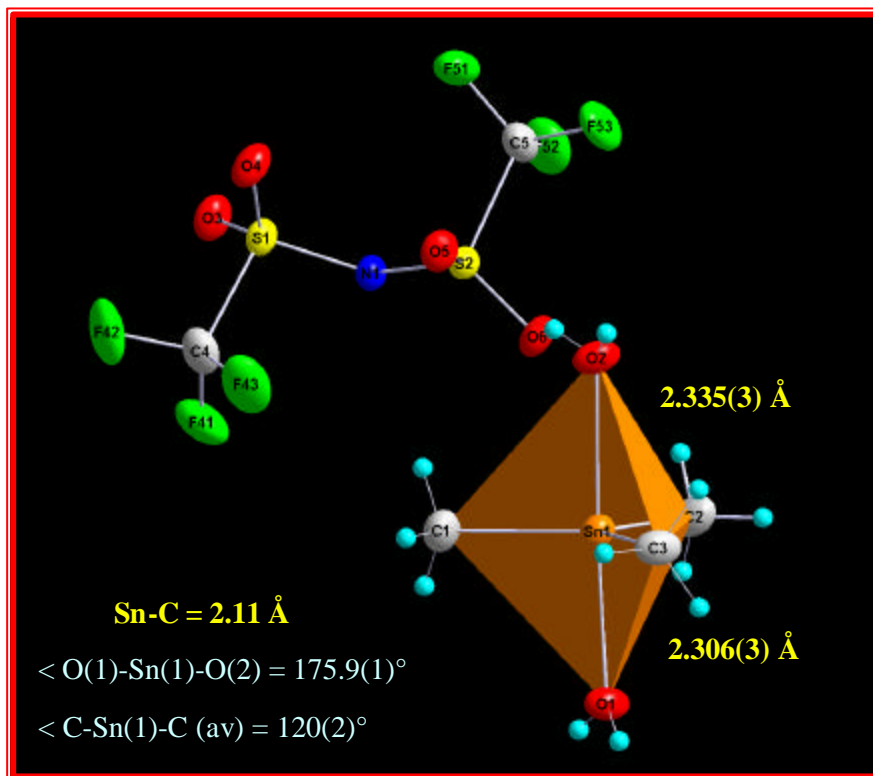
The hydrated salt can be isolated with $\text{N}(\text{SO}_2\text{CF}_3)_2$ anion but **NOT** for OTeF_5 anion.
The compound isolated after hydrolysis is $[\text{Me}_3\text{Sn}(\text{OH}_2)_2]_2\text{SiF}_6$



The hydrolysis of trimethyltin teflate results in the decomposition of the OTeF_5 group



Hydrated trimethyltin(IV) cation



Unit cell dimensions (Å)

Monoclinic ($P2_1/c$)

$a = 7.3072(1)$, $b = 13.4649(2)$,

$c = 16.821(2)$

$\beta = 98.705(1)^\circ$

Volume (Å³) = 1636.0(3) ,

$Z = 4$

$T = 213(2)$

$R1 = 0.0367$

$wR2 = 0.0736$

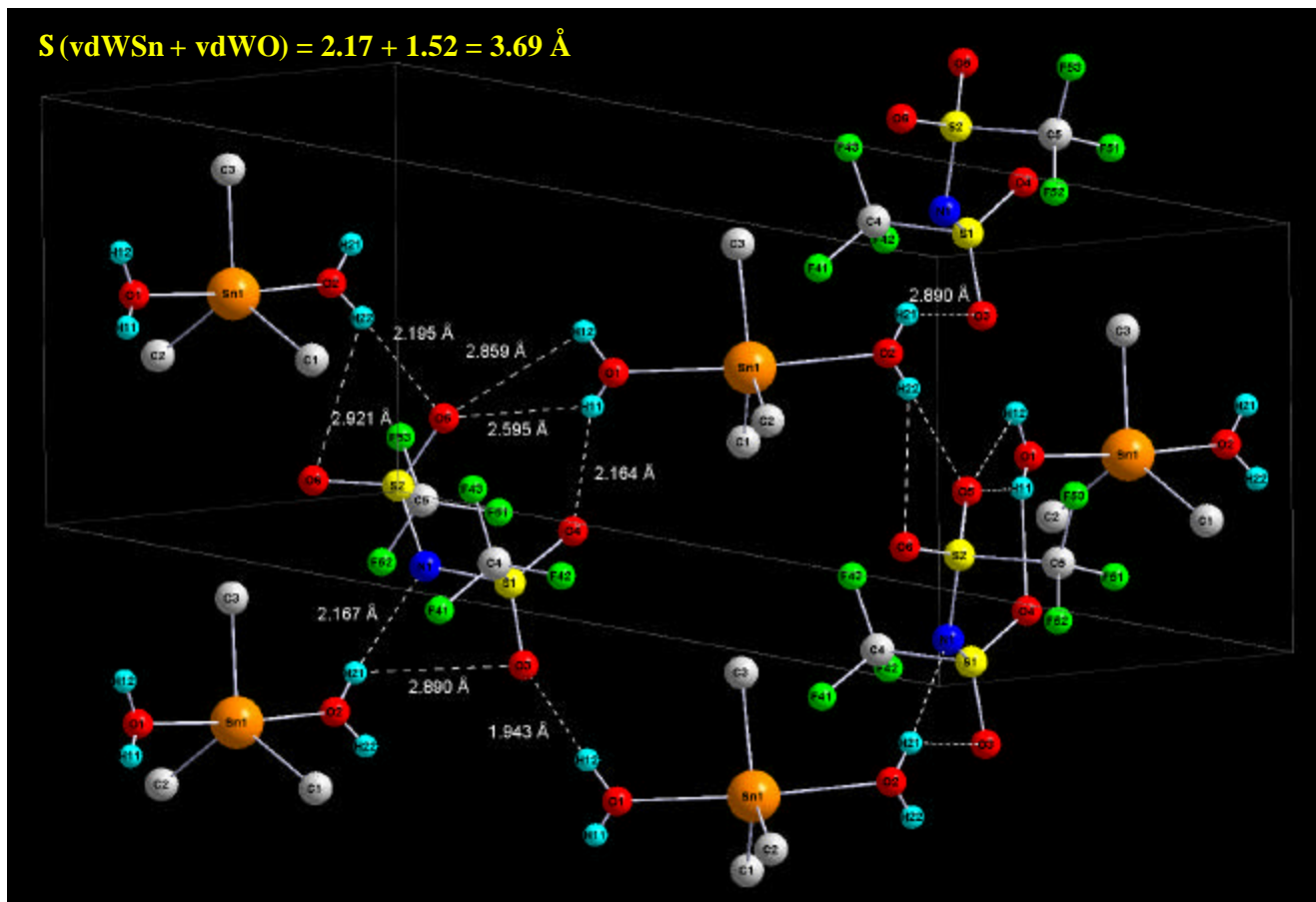
$S = 1.233$



Hydrogen bonding in hydrated trimethyltin(IV) cations



$$S(\text{vdWSn} + \text{vdWO}) = 2.17 + 1.52 = 3.69 \text{ \AA}$$

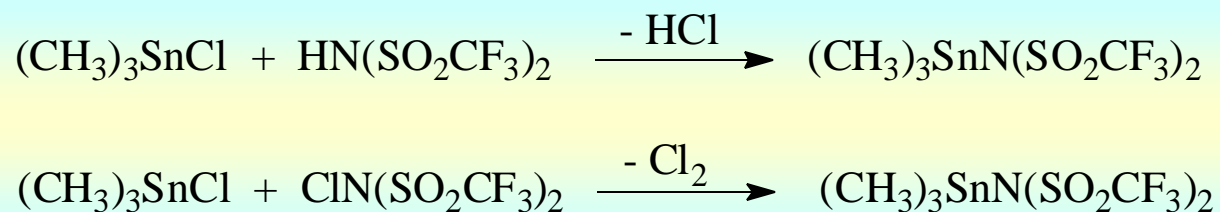




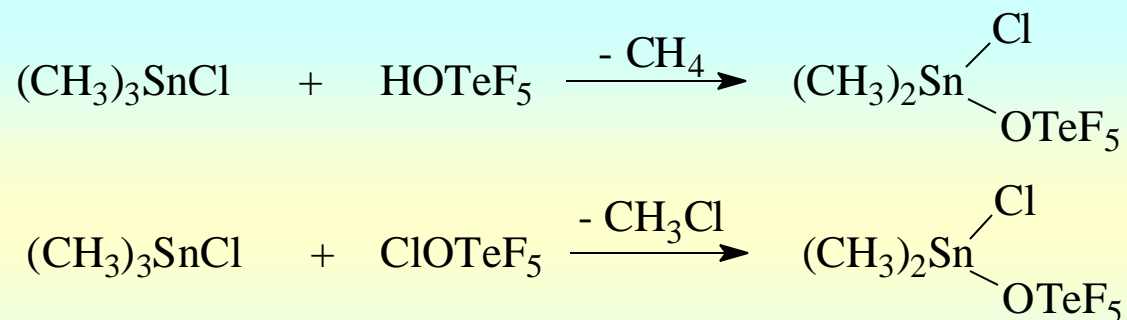
Sn-C versus Sn-Cl bond cleavage



$\text{XN}(\text{SO}_2\text{CF}_3)_2$ ($\text{X} = \text{H}, \text{Cl}$) shows a preferential Sn-Cl bond cleavage



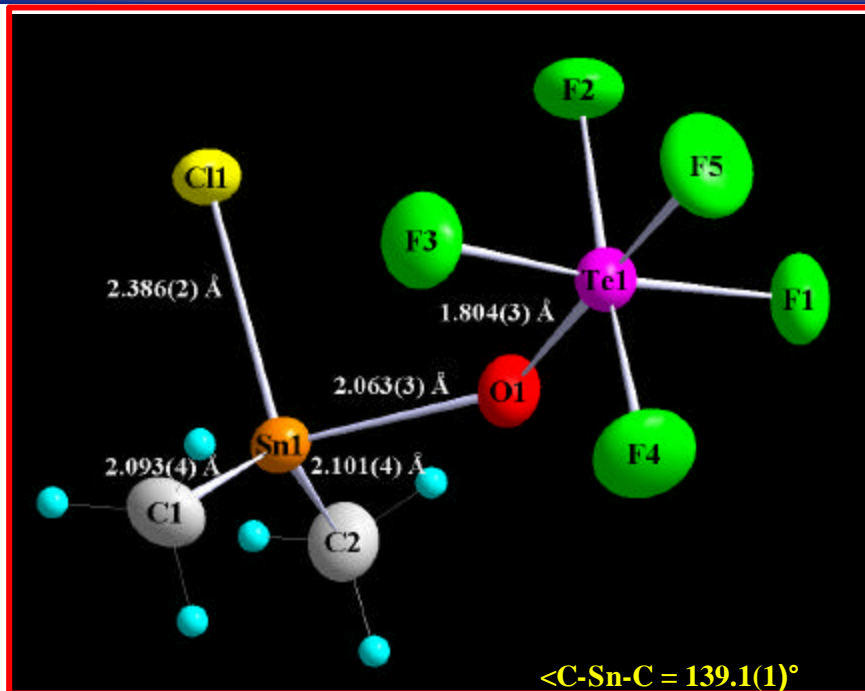
XOTeF_5 ($\text{X} = \text{H}, \text{Cl}$) shows a preferential Sn-C bond cleavage



According to Sladky and Kropshofer (*JCS Chem. Commun.*, 1973, 600), reaction of $(\text{CH}_3)_3\text{SnCl}$ with HOTeF_5 gives trimethyltin(IV) teflate exclusively!



Structure of $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{OTeF}_5$



Unit cell dimensions (\AA)

Monoclinic $P2_1/n$

$a = 5.8204(8)$, $b = 10.782(1)$,

$c = 15.493(2)$

$\beta = 99.59(1)^\circ$

Volume (\AA^3) = 971.7(2)

$Z = 4$

$T = 218(2) \text{ K}$

$R1 = 0.0282$

$wR2 = 0.0712$

$S = 1.088$

$\text{Te-O} (\text{\AA}) (\text{X}=\text{OTeF}_5) : \text{B}(\text{X})_3 = 1.874(6)$; $[\text{TBA}][\text{H}(\text{X})_2] = 1.800(4)\text{av}$; $[\text{Au}(\text{X}_3)]_2 = 1.91(2)$

Strauss et al., *Inorg. Chem.*, 1986, 25, 2806 and references therein

$n(\text{TeO}) = 856 \text{ cm}^{-1}$ in IR and Ra; $n(\text{SnO}) = 427 (\text{IR})/424 (\text{Ra}) \text{ cm}^{-1}$; $n(\text{SnCl}) = 313 (\text{Ra}) \text{ cm}^{-1}$

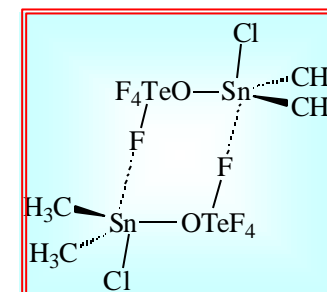
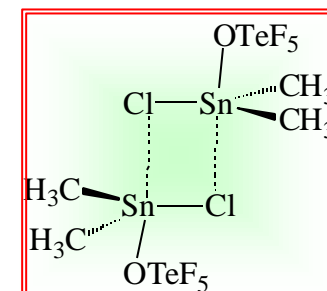
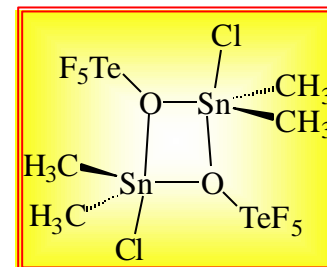


Tetra- or pentacoordinated tin???



The C-Sn-C angle calculated using $^2J(^{119}\text{Sn}-^1\text{H})$ (67.9 Hz) and $^1J(^{119}\text{Sn}-^{13}\text{C})$ (472 Hz) coupling constants for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ dissolved in CD_2Cl_2 is approximately $\sim 118^\circ$. The $d(^{119}\text{Sn})$ value of ~ 142.7 ppm indicates that tin is present in a five-coordinate environment. The fifth coordination site can be occupied by a bridging chlorine, fluorine or oxygen from a neighboring $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$ molecule.

^{119}Sn NMR show the presence of another broad peak at ~ 127 ppm, which is due to an equilibrium. In VT NMR studies using toluene- d_8 as a solvent, this peak disappears at -80°C .





Coordination environment around tin

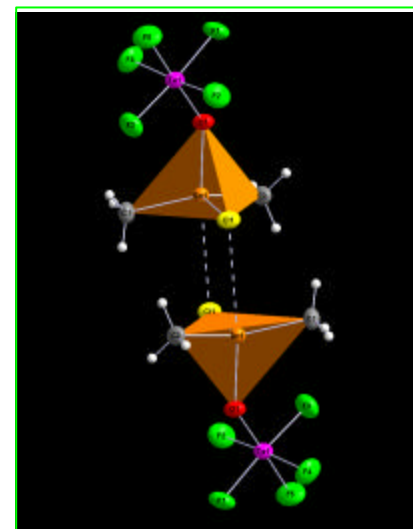
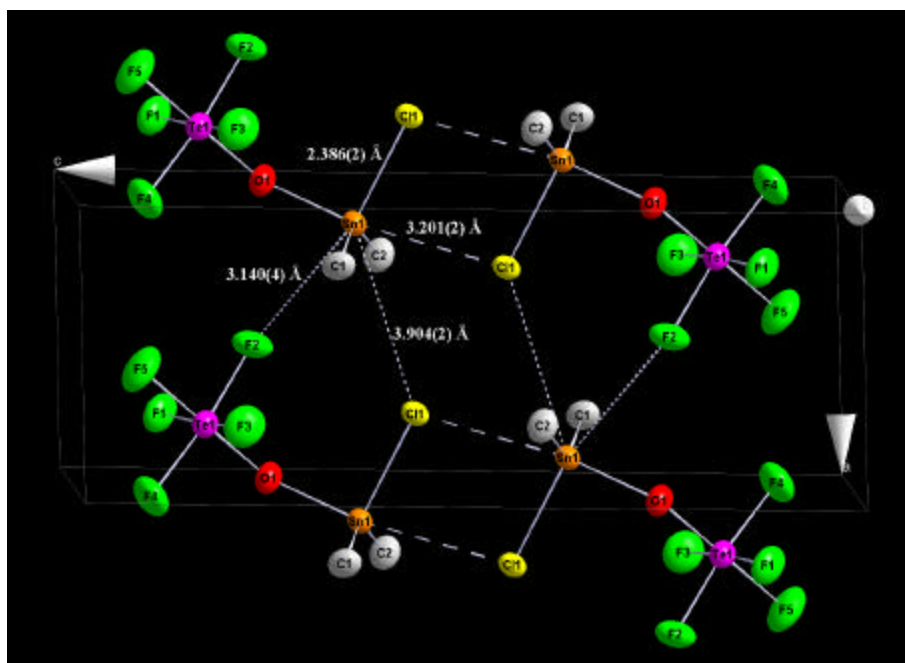


Sn-Cl contact = 3.201(1) Å

Much shorter than the sum of van der Waal radii of tin and chlorine.

A longer Sn-Cl contact is also present at 3.904(2) Å.

$$S(\text{vdWSn} + \text{vdWCl}) = 2.17 + 1.75 = 3.92 \text{ Å}$$

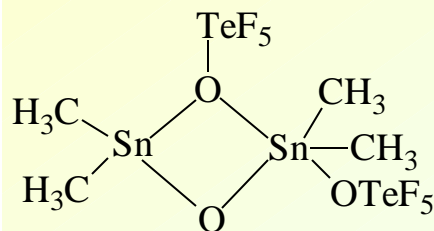
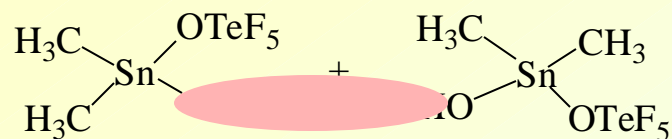
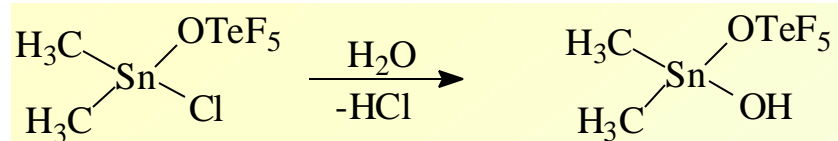


One Sn-F contact is also found in the crystal lattice 3.140(4) Å, which is much shorter than the sum of van der Waal radii of tin and fluorine.

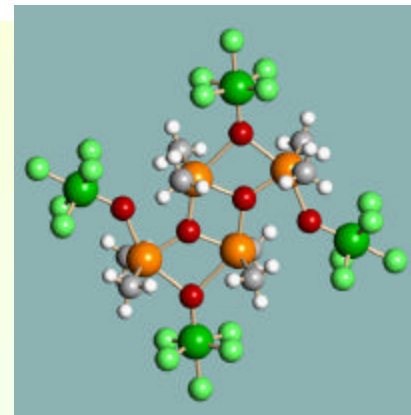
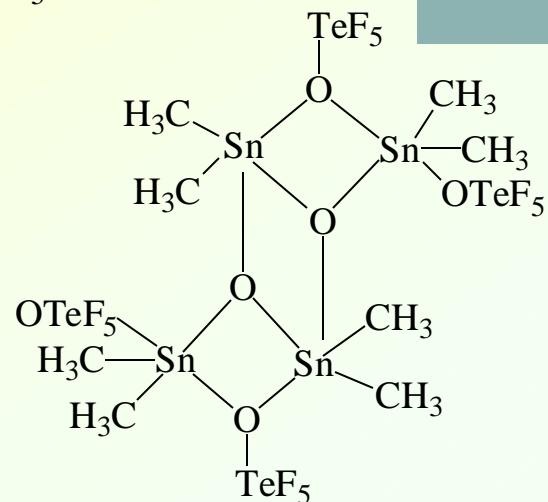
$$S(\text{vdWSn} + \text{vdWF}) = 2.17 + 1.47 = 3.64 \text{ Å}$$



Hydrolysis of the Sn-Cl bond in $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{OTeF}_5$

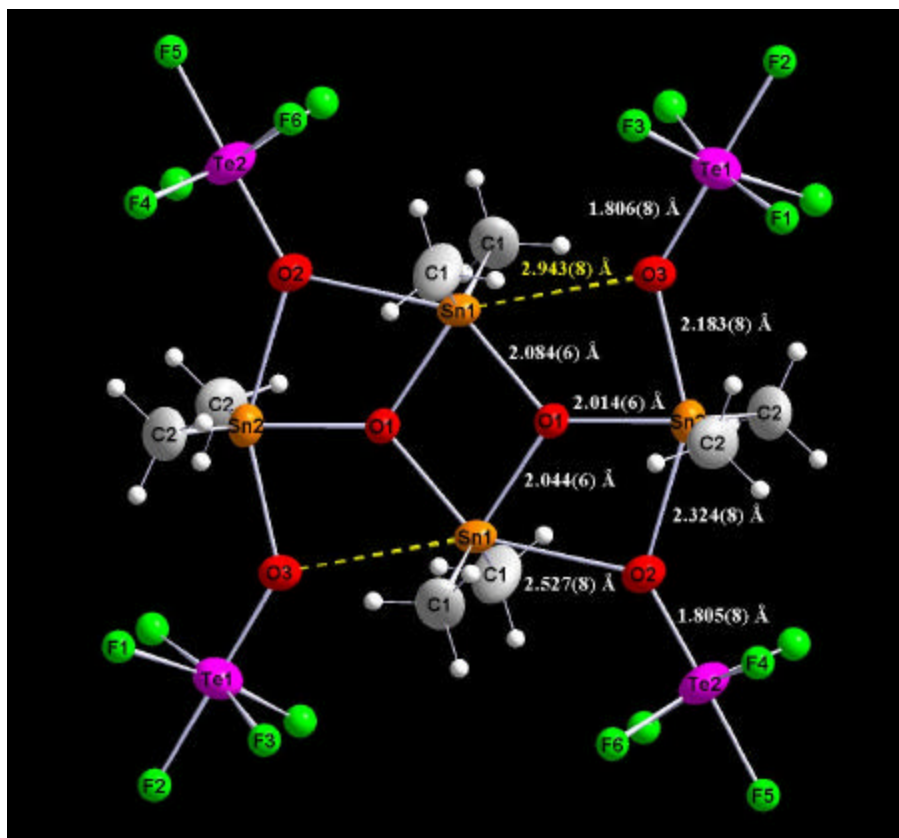


Dimerization





Structure of the dimethyloxotin(IV) teflate



Unit cell dimensions (Å)

Orthorhombic

Space Group: *Pnnm*

$a = 12.574(6)$, $b = 12.667(6)$,

$c = 11.682(5)$

Volume (Å³) = 1860.6(1)

$Z = 2$

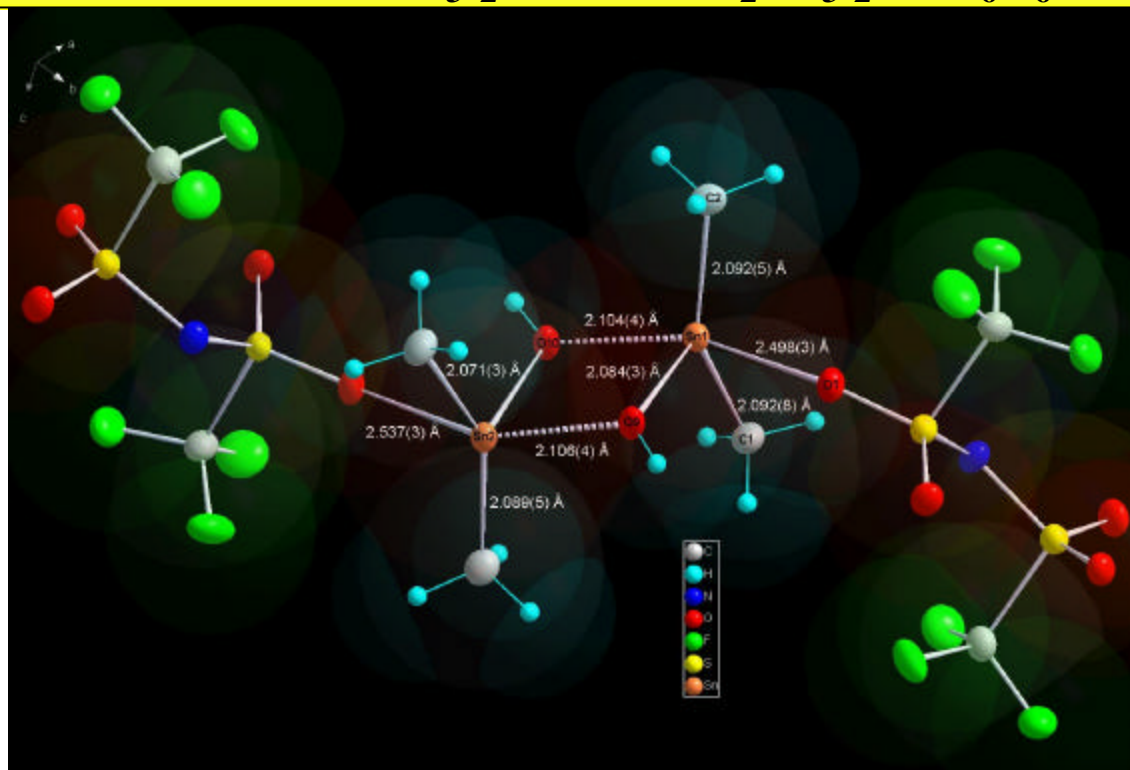
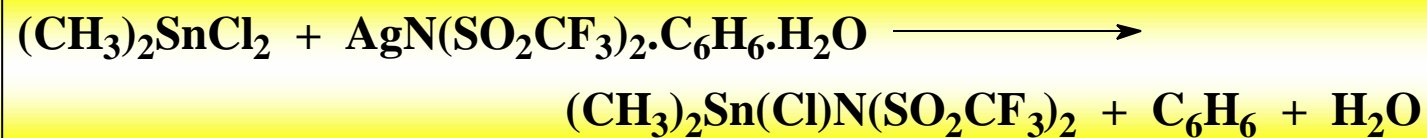
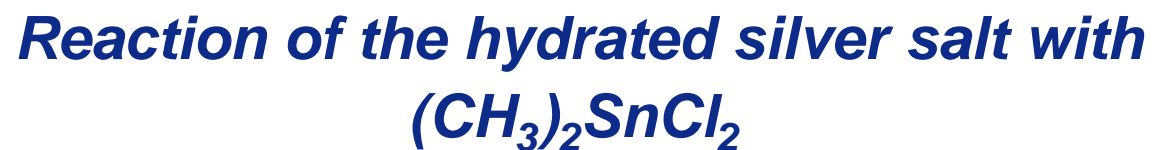
$T = 243\text{ K}$

$R1 = 0.0376$

$wR2 = 0.1021$

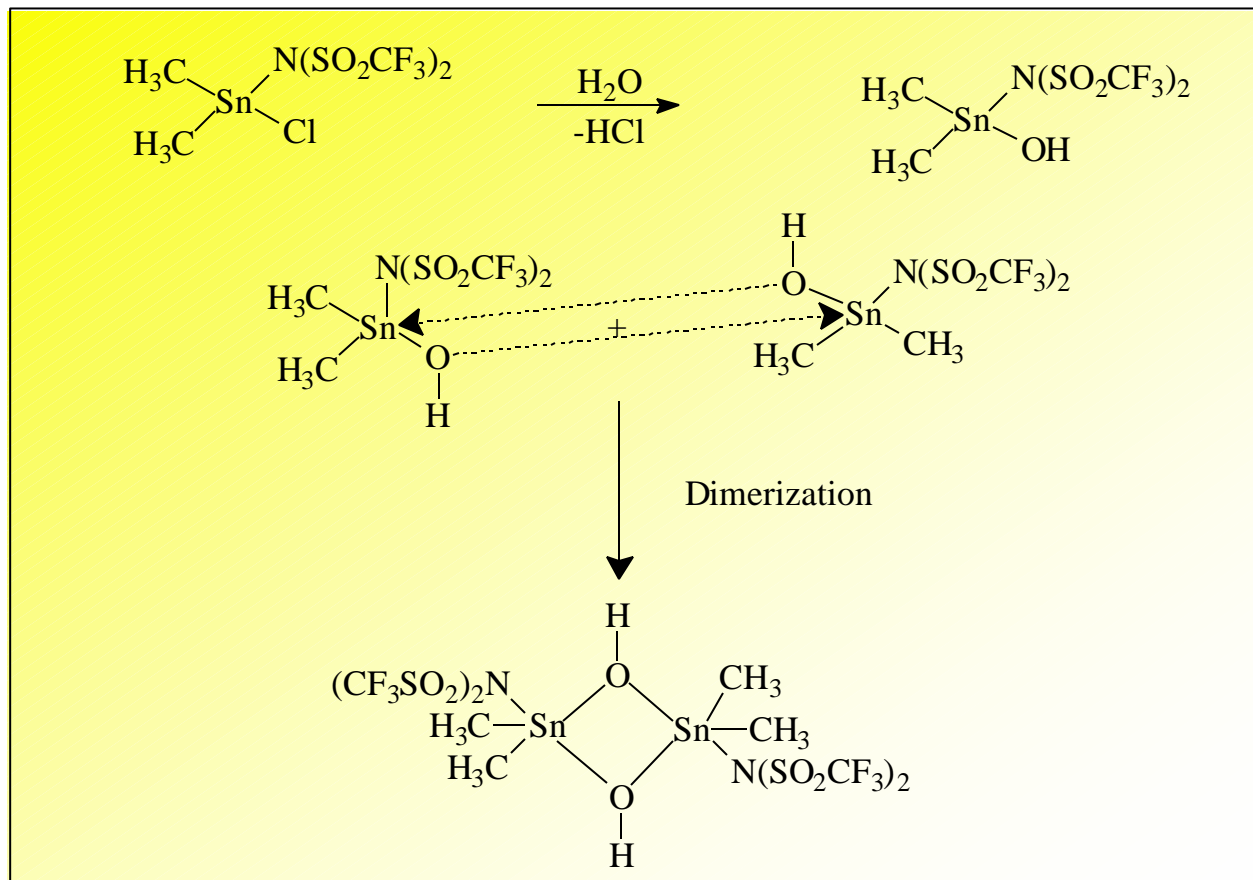
$S = 1.04$

$S(\text{vdWSn} + \text{vdWO}) = 2.17 + 1.52$
 $= 3.69\text{ Å}$





Formation of $\text{Me}_2\text{Sn}(\text{OH})\text{N}(\text{SO}_2\text{CF}_3)_2$

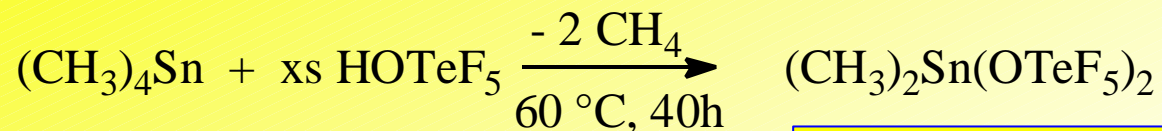




Solvolysis of Me_4Sn in excess acid: Synthesis of dimethyltin(IV) teflate

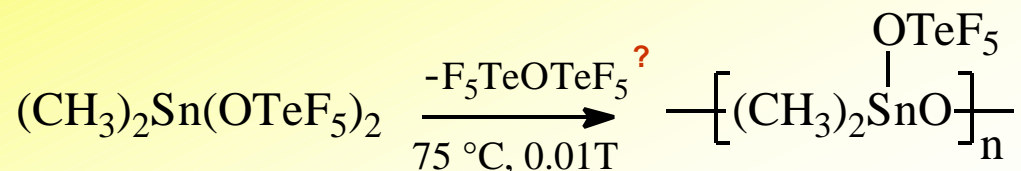


- ✓ **Dimethyltin(IV) teflate is formed when tetramethyltin is reacted with excess teflic acid**



MS shows $[\text{M}-\text{CH}_3]^+$ peak

- ✓ **Upon sublimation $\sim 75\text{ }^\circ\text{C}/0.01\text{T}$ a polymeric species is formed, probably due to the loss of $\text{O}(\text{TeF}_5)_2$**



$$n(\text{TeO}) = 877\text{ cm}^{-1}; n(\text{SnO}) = 434\text{ (IR) cm}^{-1}; n_{\text{as}}(\text{SnC}) = 591\text{ cm}^{-1}, n_{\text{s}}(\text{SnC}) = 531\text{ cm}^{-1}$$



Structure of dimethyltinooxteflate



Unit cell dimensions (Å)

Monoclinic $P2_1/n$

Rotational TWIN

$a = 7.510(6)$, $b = 15.729(12)$,

$c = 8.119(7)$

$\beta = 115.1(1)^\circ$

Volume (Å³) = 876.7(12)

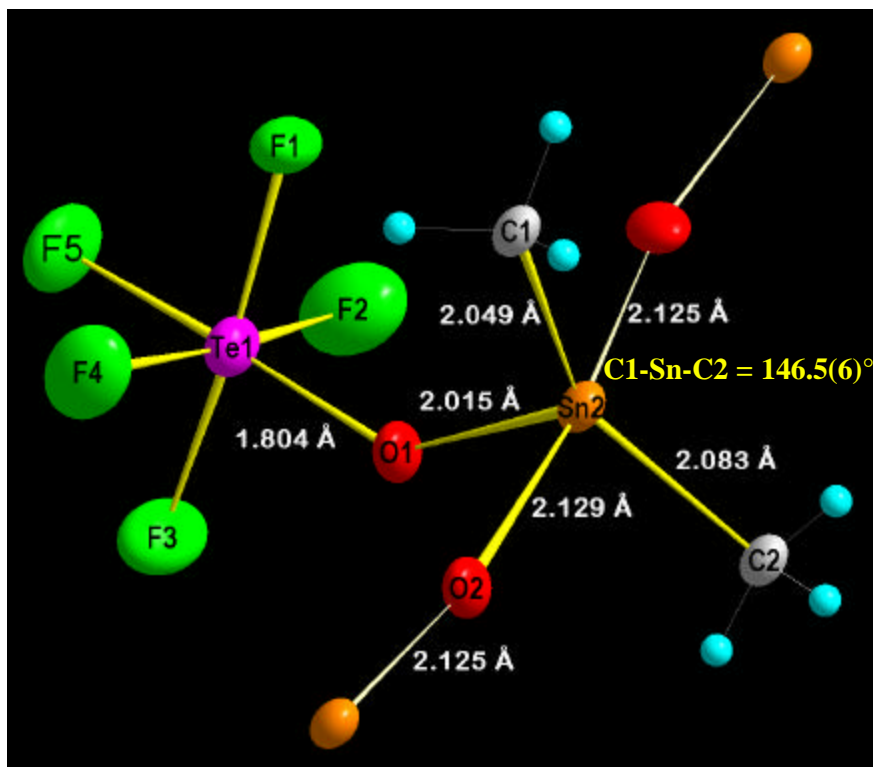
$Z = 4$

$T = 233(2) \text{ K}$

$R1 = 0.1028$

$S = 1.84$

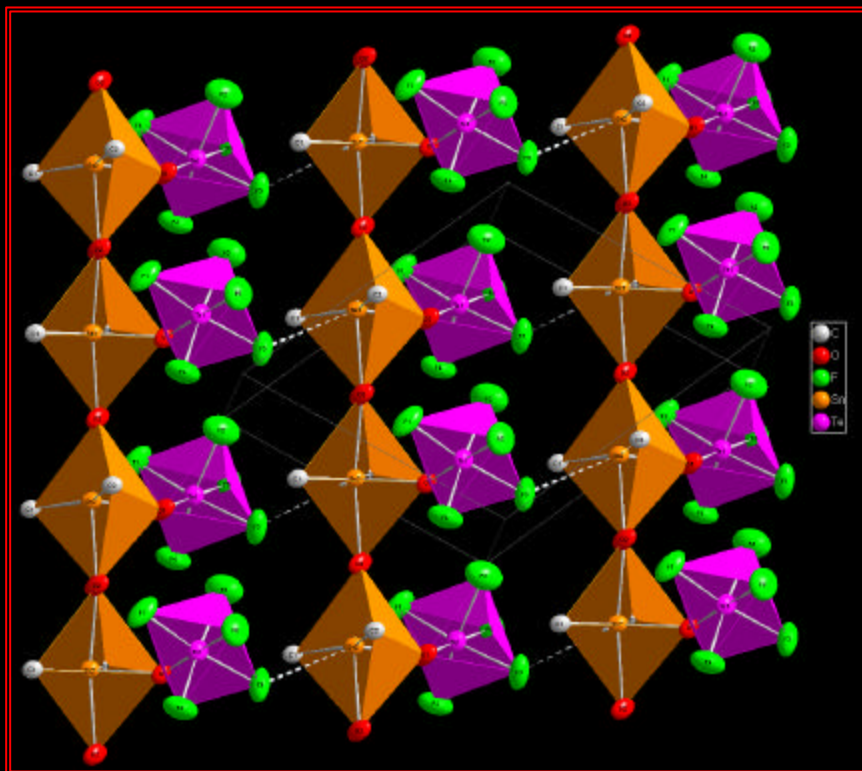
BASF = 0.256



$\text{C1-Sn-O1} = 110.2(5)^\circ$; $\text{C2-Sn-O1} = 103.3(6)^\circ$,
 $\langle \text{equi. X-Sn-X (av)} \rangle = 120^\circ$; $\text{O2-Sn-O2}^* = 169.9(5)^\circ$



Crystal packing showing tin and tellurium polyhedra



$$S_{(\text{vdwSn} + \text{vdwF})} = 2.17 + 1.47 \\ = 3.64 \text{ \AA}$$

$$\text{Sn-F distance in the crystal packing} \\ = 3.107(16) \text{ \AA}$$

The structure shows polymeric Sn-O chains bridged by a fluorine atom of the OTeF_5 group.

$$\angle \text{Sn-O2-Sn}^* = 167.2^\circ$$

$$(\text{Sn}^* = \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$$



Conclusions



- Silver salts containing the teflate and NTf form stable arene complexes. NTf conformation varies!
- ^{119}Sn NMR chemical shifts can reflect the “electrophilic strength” and relative anion basicity for a Me_3Sn (IV) compound.
- During the solvolysis of trimethyltin chloride in HOTeF_5 , there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond
- Trimethyltin(IV) teflates/F-imides are highly electrophilic in nature and form 1:1 or 1:2 complexes with donor solvents
- Chlorodimethyltin(IV) teflate hydrolyzes to form a Sn-O ladder compound and sublimation of dimethyltin(II) bis(teflate) results in the formation of an oxo-bridged species.
- Use of hydrated silver salt to prepare methyltin derivatives results in the hydrolysis of trimethyltin derivative to form hydrated tin cation.
- Chlorodimethyltin NTf hydrolyzes to form the μ -(hydroxo) species, where NTf is in a *trans* orientation



Conclusions



- Trimethyltin(IV) derivatives can easily be prepared by the reaction of acids with excess tetramethyltin
- Trimethyltin(IV) derivatives are highly electrophilic and coordinate with solvents giving trigonal bipyramidal geometry
- In case of water and DMSO, ionic salts are formed with two donor molecules occupying the axial position
- During the solvolysis of trimethyltin chloride in HOTeF_5 , there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond
- Chlorodimethyltin(IV) teflate hydrolyzes to form a Sn-O ladder compound.
- The sublimation of dimethyltin(II) bis(teflate) results in the formation of an oxo-bridged species.



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BACKUP/SUPPL. SLIDES



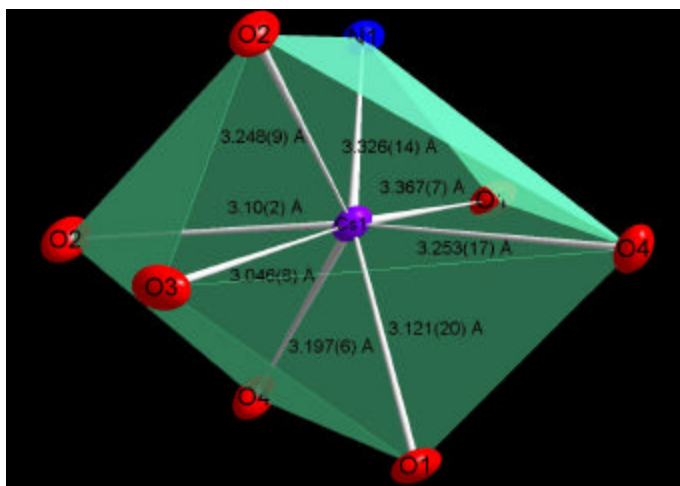
BACKUP



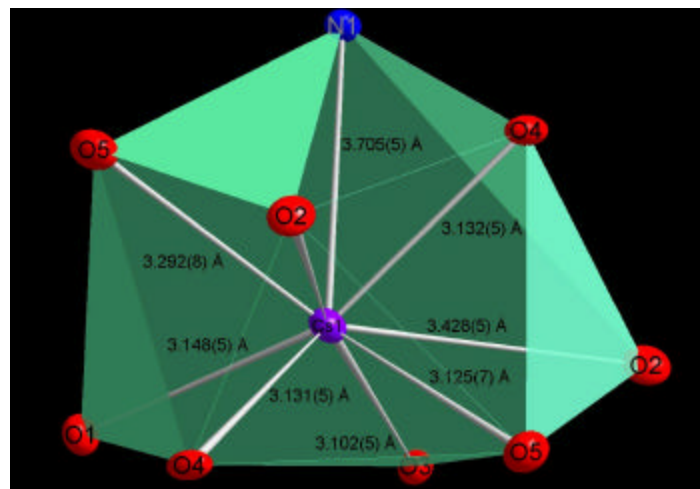
Coordination environment of Cs in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Octa-coordinated with a short Cs-N bond



Nona-coordinated with a long Cs-N bond

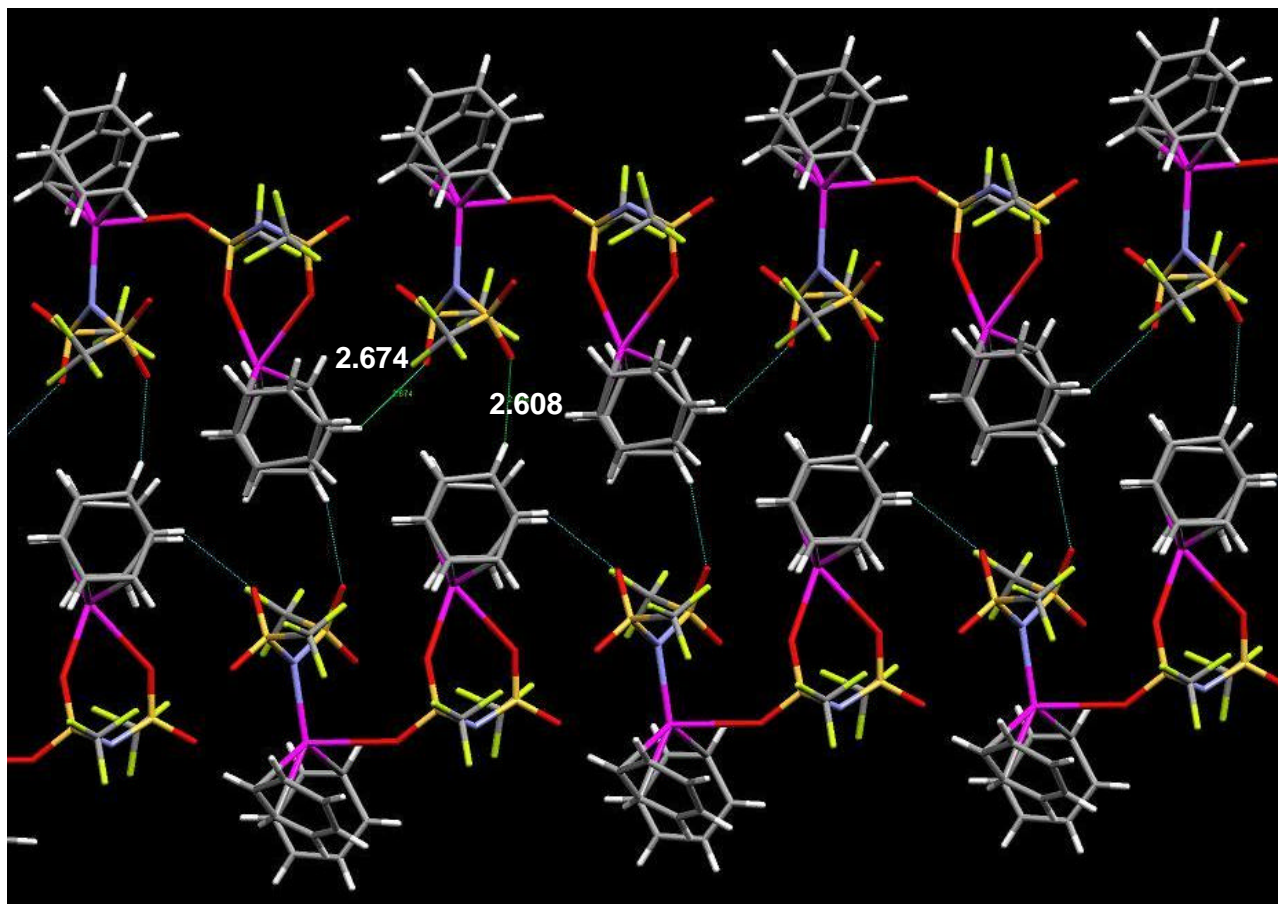


$\text{CsN}(\text{SO}_2\text{CF}_3)_2$ is reported to be ten-coordinated

DesMarteau, Pennington *et al.*, Solid State Sciences, 2002, 4, 1535-1545



Crystal packing in $[AgN(SO_2CF_3)_2(C_6H_6)_2]$



14th European Symposium on Fluorine Chemistry, July 11-16, Poznań, Poland
Distribution A Statement: Approved for public release; distribution unlimited



Bond distances and angles $\text{Me}_2\text{SnClOTeF}_5$



•	Sn(1)-C(2)	2.104(4)		
•	Sn(1)-C(1)	2.115(4)		
•	Sn(1)-C(3)	2.120(4)		
•	Sn(1)-O(1)	2.306(3)		
•	Sn(1)-O(2)	2.335(3)		
•	S(1)-O(3)	1.427(2)		
•	S(1)-O(4)	1.428(3)		
•	S(1)-N(1)	1.573(3)		
•	S(1)-C(4)	1.825(5)		
•	S(2)-O(6)	1.421(3)		
•	S(2)-O(5)	1.433(3)		
•	S(2)-N(1)	1.589(3)		
•	S(2)-C(5)	1.844(4)		
			C(2)-Sn(1)-C(1)	117.8(2)
			C(2)-Sn(1)-C(3)	120.1(2)
			C(1)-Sn(1)-C(3)	122.1(2)
			C(2)-Sn(1)-O(1)	89.83(15)
			C(1)-Sn(1)-O(1)	92.3(2)
			C(3)-Sn(1)-O(1)	87.19(13)
			C(2)-Sn(1)-O(2)	91.04(15)
			C(1)-Sn(1)-O(2)	90.8(2)
			C(3)-Sn(1)-O(2)	88.95(13)
			O(1)-Sn(1)-O(2)	175.94(11)
			O(3)-S(1)-O(4)	118.5(2)
			O(3)-S(1)-N(1)	107.6(2)
			O(4)-S(1)-N(1)	116.1(2)
			O(3)-S(1)-C(4)	104.0(2)
			O(4)-S(1)-C(4)	105.4(2)
			O(6)-S(2)-O(5)	118.2(2)
			O(6)-S(2)-N(1)	109.0(2)
			O(5)-S(2)-N(1)	115.3(2)
			O(6)-S(2)-C(5)	104.7(2)
			O(5)-S(2)-C(5)	105.0(2)
			S(1)-N(1)-S(2)	125.3(2)